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## **Prerequisites to Development of Reduction Process in Heavy Non-Ferrous Metal Metallurgy**

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*Essence of upgrading to process heavy non-ferrous metal sulfide concentrates and of reduction operations has been analyzed. Their environmental hazards have been shown. A landmark solution for metal reduction immediately from sulfide compounds is proposed.*

*Keywords: reducing properties of sulfide sulfur, melt of caustic soda, metal reduction in “metal sulfide-NaOH” system.*

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## **Предпосылки совершенствования восстановительных процессов в металлургии тяжелых цветных металлов**

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*Проанализирована сущность обогатительных процессов переработки сульфидных концентратов тяжелых цветных металлов, а также восстановительных операций. Показаны источники экологической опасности их осуществления. Предложено принципиально новое решение восстановления металлов непосредственно из сульфидных соединений.*

*Ключевые слова: восстановительные свойства сульфидной серы, расплав каустической соды, восстановление металла в системе «металл – сульфид – NaOH».*

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### **Introduction**

Global production of heavy non-ferrous metals from mineral raw materials is based on energy-intensive processes involving considerable impacts on the ecosystem and aggravation of global problems. In this connection it is topical to review certain technological conversions to find new process solutions.

The challenge of metallurgical production is to produce metals from chemical compounds of mineral or technological origin. Industrial metallization is, at this, oriented to reduce from oxygen compounds employing carbon- and sulfur-containing reagents.

Principal source for production of heavy non-ferrous metals are sulfide mineral raw materials. Target component content in ores (0.5–5%) considered, the production process of heavy metals can be presented as a chain of successive upgrading operations providing 100...10-fold concentration of target elements involving various techniques. In general terms the block diagram of the process is shown in Fig. 1.

Flotation concentration is implemented in water pulps containing soluble and insoluble reagents interacting with mechanically exposed surface of mineral grains to chemically activate hydrophobic property and by air lift efficiently extract hydrophobic components into concentrates. Among them are sulfide lead concentrates (35–75% lead), copper (from 15 to 40% copper), nickel (from 8 to 15% nickel) in satisfactory extraction (85–95%). Concentrates accumulate from 60 to 80% sulfur present in the concentrates. The rate of enrichment by flotation is 10–15 times with production of final tailings.

In addition to target mineral forms sulfide concentrates of non-ferrous metals are primarily specified by presence of the iron-containing components. Current metallurgical enrichment of sulfide

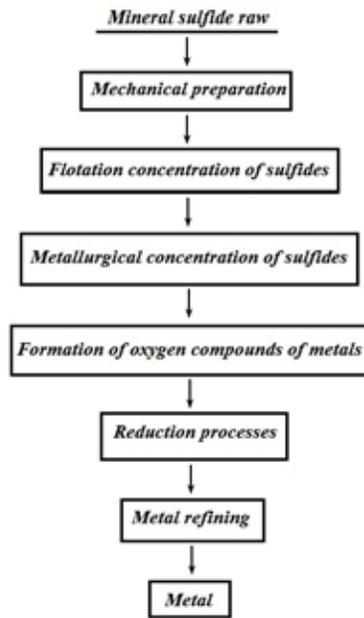


Fig. 1. Processing of mineral raw materials of heavy non-ferrous metals

products involves oxidative decomposition of sulfide iron compounds (roasting, conversion) to form condensed iron-silicate products (slag) and gaseous sulfur-containing compounds.

Metallurgical enrichment is dictated by the need to improve the concentrate quality in terms of target components in restructuring the mineral forms. Heavy non-ferrous metallurgy mostly employs high-temperature processes [1].

Metallurgical enrichment of sulfide concentrates involves use of oxygen and fluxes and is specified by in-depth changes in the composition of products containing the target component. These processes provide for concentration rate 1.5-2 and form several phases, one of them contains the extracted metal (metals) in the form of a sulfide alloy, the other – alloys of silicates, primarily iron, and the third – gaseous substances – sulfur oxides.

### Reduction process

Metallurgical enrichment produces sulfide and sulfide-metallic phases of lead, copper, nickel and cobalt with target component content from 60 to 70%. The said enriched materials form by matte conversion to produce “white matte”, nis matte and its separation products [2, 3].

After the target component containing product is metallurgically enriched it is converted involving formation of metal-oxygen compounds. Oxidative treatment of melts (Cu) or solid sulfides (Ni, Pb) concurrently forms sulfur-containing gaseous products ( $SO_2$ ,  $SO_3$ ). Usually, at this conversion the target metal in the product undergoes slight quantitative changes:



The practice of metal reduction from oxygen compounds is to use for electron donors, first of all, carbon-containing reagents (metallurgical coke, hydrocarbons), to a lesser degree – hydrogen, reagents of metal origin (iron, aluminum, etc.) and sulfide sulfur. Reduction of heavy non-ferrous metals involving carbon and hydrocarbonic reducing agents can be implemented in solid-gas, melt of chemical metal compounds-gas or melt of chemical compounds-solid systems with corresponding production of gaseous oxygenates of reducing reagent [1]. Chemism of metallization processes is as follows:



Properties that define these processes are that because of their thermodynamics and kinetics they are realized under high temperature conditions (higher than 1000 °C). As a result molten metallic phase and gaseous product form. When carbon reducing agents are used the gaseous phase contains primarily oxygen-carbon compounds, and in case of hydrocarbonic – carbon oxides and water vapor.

Reducing properties of sulfide sulfur [1] realize in a condensed system involving oxygen compounds of the metal being reduced and the melt of its sulfide. The process is, at this, combined with oxidation of a part of sulfides and, accordingly, with heat production heating the system, melting of its components and metallization reaction. Reduction is realized under high temperature conditions (1100–1600 °C) and is accompanied by gas emission. The gaseous phase contains in its composition sulfur dioxides. Chemism of the process is described by the following equation:



Sulfide sulfur can be efficiently used as a reducing agent to metalize copper from its oxide. The process runs to its completion. Lead reduction, in its turn, from the oxide by the lead sulfide is realized partially only (not more than 50%). Therefore, in addition to sulfide sulfur its realization involves participation of carbon. Such a mixture of reagents provides for metallization approaching 100%. Nickel can assumingly be reduced from its oxide by sulfide sulfur only at temperatures above 1600 °C.

### Theoretical framework of reduction processes

Fundamental scientific notions about reduction of metals from oxides were formulated by Academician A.A. Baikov [4]. Their essence is to realize dissociative processes involving formation of elementary substances in corresponding aggregate states:



With decrease of oxygen content in the system equilibrium (6) can shift right, e.g. with addition of a reagent capable of intensively interacting with it, e.g. of carbon or hydrocarbonic origin.

The process can be realized only at very high temperatures, when the probability of dissociation of metal oxides should increase. According to numerous authors [4, 5], the pressure of metal oxide dissociation over a broad temperature range with few exceptions (Ag<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, CuO), are so insignificant, that to measure them directly it is difficult, and in many cases – impossible.

For purposes of metal reduction from oxides by gaseous agents (CO, H<sub>2</sub>), adsorption- autocatalytic theory [6, 7] has been developed; by this theory determinant is the adsorption of reducing gas on the reactive surface of the oxide facilitating separation of oxygen from the oxide to interact with adsorbed gas. As a result, gaseous product with new composition and metallic phase form. The final phase of the process is desorption from the metal surface of the oxygen compound – conversion product of the reducing agent.

The processes of metal reduction from their sulfides enjoy less attention than the oxygen compounds. There is a good consensus of opinion that the reduction processes should be based on sulfide dissociation reactions and for them hold analogous regularities as for the oxides. Common is the approach proposed by A.N. Volsky and Ye.M. Sergievskaya [8] for decomposition of iron sulfide involving reaction of iron and sulfur atomization:



According to equation (7) the probability of reducing iron from its sulfide under normal conditions is very small, which is proved by value  $\Delta G^0$  equal to 101.9 kJ/mol [8].

Analysis of theoretical notions about reduction of metals from oxides and sulfides allows for the conclusion that:

- the process should be extremely energy intensive;
- improvement of the said notions employing adsorption-autocatalytic provisions allows to count on certain decrease of energy consumption;
- the history of existence of the concept of A.A. Baikov with proper amendments if fairly long, but it is not proved by reliable experimental data;
- proposed theoretical prerequisites deny formulating principles of controlling the reduction processes;
- electrochemical notions about metal reduction [9] from solids can be considered qualitative.

The electrochemical essence of the reduction process becomes dominant is does not depend on the nature of the metal reduced and its coordination environment, neither on the aggregate state of the initial substance (solid or liquid). From the standpoint of modern ion-covalent knowledge about the nature of forces taking part in formation of a substance, metal oxides and sulfides can be considered compounds of oppositely charged particles, forming by the totality of electrostatic and covalent binding in  $Me^{z+} - S^{2-}$  system. The ion-ion interactions belong, at this, to the long-range order. The covalent (donor-acceptor) interactions, in their turn, are predominantly associated with redistribution of electrons from ligands to the metal to form corresponding orbitals and with respect to the metal ion formally exhibit reduction function [2, 3]. Such type of interaction can be responsible for development of redox processes when the metal ion and ligand are considered as a short-circuit electrode pair in internal electrolysis. The metal ion performs, at this, the function of cathode, and sulfide-ion – of anode. Under certain conditions excessive negative polarization of metal ion and excessive positive polarization of ligand may be eliminated with emergence of new quality – uncharged metal atom and uncharged sulfur atoms.

These assumptions allowed for the conclusion about possibility of emergence of metal ion-ligand electrode pair which under certain conditions can operate in short-circuit mode. The donor-acceptor bonding in  $Me^{z+} - S^{2-}$  system is considered as a prerequisite to development of redox interactions

to form qualitatively new products – solid, liquid and gaseous ( $\text{Me}^0$ ,  $\text{S}^0$ ). Important, at this, are the potentials of electron bonding by metal ions and electron donor potentials of sulfide ion.

Operation of the electrochemical system becomes really possible when the closed electrode pair is submerged into some medium – condensed or gaseous. This medium provides for the assimilation of internal electrolysis products. The prerequisite to internal electrolysis involving short-circuited electrode pair is the difference in electron donor and electron acceptor possibilities of the ligand and metal ion.

For metal sulfides the electron donor function of sulfide sulfur is essential and is provided for by 3d-electrons with formation of corresponding orbitals involving metal ions. As compared to the oxygen anion, sulfide sulfur is viewed as expressed reducing agent, which is proved by considerable negative potential of anode depolarization ( $-0.48$  V [10]).

Action of short-circuited  $\text{Me}^{z+}-\text{S}^{2-}$  electrode pair results in two phases – metal with sulfur adsorbed on its surface. This electrode pair is realized when the medium where it is submerged provides for bonding of sulfur, e.g. to transfer it to the lower or higher oxidation level and to form stable, e.g. oxygen compounds.

We assumed that qualitative change in the essence of reduction processes is possible providing the use of condensed media containing reagents bonding the resulting element sulfur. Of special interest for electrochemical transformations is the melt of caustic soda [11]. The choice of the said medium was not random. Sodium hydroxide has both reactive and salvation capacities with respect to a series of sulfur-containing compounds, is specified by melting temperature  $330$  °C and is indifferent to the newly forming metallic phase [12]. The alkali is capable of provoking disproportionation of  $\text{S}^0$  with accumulation of associated products containing sulfide, polysulfide, thiosulfate, sulfite and sulfate sulfur and their salvation [13].

Table 1 presents Gibbs energy changes for several possible  $\text{S}^0$  disproportionation reactions distinct in accumulation in the system in addition to  $\text{S}^{2-}$  of polysulfide ions and sulfur in oxidation states +6, +4 and +2. From the Table it follows, that most thermodynamically probable is the process forming sulfide and sulfate sulfur.  $\Delta G$ , at this, essentially depends on temperature. These sulfur

Table 1.  $\Delta G$  of element sulfur disproportionation reactions in alkaline medium, kJ/g-sulfur atom [14]

T, K	№	298	573	773	873	973	1073	1173	1273
$2\text{NaOH} + \text{S} = 0,75\text{Na}_2\text{S} + 0,25\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	(8)	-58.4	-80.4	-92.9	-98.8	-104.9	-111.1	-117.5	-124.4
$2\text{NaOH} + \text{S} = 0,667\text{Na}_2\text{S} + 0,333\text{Na}_2\text{SO}_3 + \text{H}_2\text{O}$	(9)	-45.1	-63.9	-69.1	-69.9	-70.1	-69.6	-68.5	-67.0
$1,5\text{NaOH} + \text{S} = 0,5\text{Na}_2\text{S} + 0,25\text{Na}_2\text{S}_2\text{O}_3 + 0,75\text{H}_2\text{O}$	(10)	-27.6	-28.3	-21.7	-16.9	-11.4	-5.3	1.1	8.1
$7\text{S} + 8\text{NaOH} = 3\text{Na}_2\text{S}_2 + \text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O}$	(11)	-40.6	-55.4	-57.7	-59.2	-60.3	-61.3	-62.1	-62.9
$10\text{S} + 8\text{NaOH} = 3\text{Na}_2\text{S}_3 + \text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O}$	(12)	-35.8	-41.8	-41.3	-40.8	-40.1	-39.2	-38.2	-37.4
$13\text{S} + 8\text{NaOH} = 3\text{Na}_2\text{S}_4 + \text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O}$	(13)	-25.4	-31.9	-33.1	-33.2	-33.2	-33.1	-32.9	-32.8

conversion reactions make reduction processes involving metals irreversible at relatively low temperatures.

*Thermodynamic studies of metal reduction from sulfides in NaOH melt*

Tables 2–6 show results of thermodynamic studies of reduction of lead, copper, nickel, cobalt and iron from sulfide compounds by sulfur proper in the presence of sodium hydroxide as the process medium (melting temperature 330 °C ).

Redox reactions in  $Pb^{2+} - S^{2-}$  system can be successfully realized to form the metallic phase and sulfite and sodium sulfate over a broad temperature range (Table 2).

As it follows from Table 2, metallization of lead directly from the sulfide compound employing electron donor properties of  $S^{2-}$  and forming sulfate sulfur as disproportionation product, is possible at temperature 700 K and higher, and as sulfate sulfur – at temperature 900 K and higher.

It seems likely, that irrespective of metal nature the reduction process runs in two stages:

- redox reaction proper with production of metal and element sulfur;
- utilization of the element sulfur by the process medium.

Chemism of the reduction process is, on the whole, aimed to produce sulfide and sulfite sulfur. In the case of formation of thiosulfate sulfur it is becoming unlikely (Table 2). One of the factors affecting chemism implementation is the content of free alkali in the system. Deficiency of the latter affects the oxidation rate in the final product.

Table 3 presents  $\Delta G$  of reactions of copper reduction from sulfide compounds ( $Cu_2S$ ,  $CuS$   $CuFeS_2$ ) in temperature range 298 – 1273 K. The said sulfides are specified by some difference in standard energy of formation:  $Cu_2S$  – minus 86.3 kJ/mol (minus 43.15 kJ/g-sulfur atom),  $CuS$  – minus 53,6 kJ/mol and  $CuFeS_2$  – minus 178.9 kJ/mol.

As it follows from Table 3, reduction of copper from covellite is possible over the entire studied temperature range. Situation is similar when copper is reduced from  $CuFeS_2$  (copper pyrite). Calculation of  $\Delta G$  of copper reduction from  $Cu_2S$  (chalcocite) is specific for little effect of temperature on variation of free energy of the redox reaction. Stoichiometric ratios  $NaOH/Cu_2S$  and  $NaOH/CuS$  are two, and for  $NaOH/CuFeS_2$  – four, which is significant for the arrangement of the reduction process.

Reduction properties of sulfide sulfur with respect to nickel and cobalt ions belonging to chalcogenides are confirmed by data on  $\Delta G$  of redox reactions (Table 4). In our studies we used

Table 2.  $\Delta G$  of reactions of lead reduction from sulfide in alkaline medium\*

№	Reaction	$\Delta G$ , kJ/mol, at temperature:								
		298	598	698	798	898	998	1098	1198	1273
(14)	$PbS+2NaOH=$ $=Pb+0,25Na_2SO_4+0,75Na_2S+H_2O$	45,0	4,9	-3,9	-12,1	-19,8	-27,0	-34,0	-41,2	-46,9
(15)	$PbS+2NaOH=$ $=Pb+0,3Na_2SO_3+0,7Na_2S+H_2O$	56,8	16,3	7,9	0,4	-6,6	-13,1	-19,3	-25,3	-30,4
(16)	$PbS+1,5NaOH=Pb+$ $+0,25Na_2S_2O_3+0,5Na_2S+0,75H_2O$	63,1	34,1	28,2	22,8	18,0	13,6	9,6	5,8	2,9

\* From now on the calculus has been made with HSC Chemistry 5.11 software

essentially different sulfides of nickel and cobalt, specifically, millerite (NiS), Heazlewoodite (Ni<sub>3</sub>S<sub>2</sub>), vaezite (NiS<sub>2</sub>). NiS<sub>2</sub> compound is understood as NiS·S<sup>0</sup> association, Ni<sub>3</sub>S<sub>2</sub> – as Ni<sup>0</sup>·2 NiS association. Attachment of nickel atom to two NiS molecules, as one sulfur atom to NiS molecule seems to increase stability of compounds. From Table 4 it is apparent that certain probability of nickel and cobalt reduction increases with sulfur content in the compound. K

Reduction of nickel from disulfide is possible as early as at temperature higher than 298 K, from monosulfide – higher than 570K, and from Ni<sub>3</sub>S<sub>2</sub> – at temperature higher than 800 K. In the case of cobalt reduction the metallic phase can form from disulfide at temperature higher than 600 K, and from monosulfide – higher than 700 K.

In the context of interaction of pyrite and pyrrhotine with alkali we studied feasibility of reduction processes. From thermodynamic calculations (Table 5) it follows, that most probable in exchange interaction of pyrrhotine with alkali is formation of iron oxide, and for pyrite – all three assumed substances (Fe, Fe(OH)<sub>2</sub>, FeO) with predominant probability of oxide formation.

Thermodynamics of pyrite, arsenic pyrite and pyrrhotine was studied in alkaline media under conditions of exchange interactions at temperature 350 °C (Table 6) [15]. From the data obtained it follows that the dissociation processes involving pyrite and with formation of hydroxide and oxide of ferrous iron (25), (26), sodium sulfide and element sulfur at the given temperature are

Table 3. ΔG of reactions of direct copper reduction from sulfide compounds in alkaline medium

№	Reaction	ΔG <sup>0</sup> , kJ/mol at temperature, K:							
		298	573	773	873	973	1073	1173	1273
(17)	Cu <sub>2</sub> S + 2NaOH = = 2Cu + 0,75Na <sub>2</sub> S + 0,25Na <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O	22.6	6.6	1.3	-6.9	-7.9	-8.6	-9.1	-10.2
(18)	CuS + 2NaOH = = Cu + 0,75Na <sub>2</sub> S + 0,25Na <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O	-6.9	-31.9	-43.3	-51.5	-56.8	-61.7	-66.5	-71.8
(19)	2CuFeS <sub>2</sub> + 8NaOH = 2Cu + + 2FeO + 3,5Na <sub>2</sub> S + 0,5Na <sub>2</sub> SO <sub>4</sub> + 4H <sub>2</sub> O	46.5	-9.6	-41.0	-54.0	-64.8	-74.3	-83.0	-92.1

Table 4. ΔG of nickel and cobalt reduction reactions in alkaline medium, kJ/g-Me atom

№	Reaction	ΔG <sup>0</sup> at temperature, K:							
		298	598	698	798	898	998	1198	1273
(20)	4NiS + 8NaOH = 4Ni + 3Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>4</sub> + 4 H <sub>2</sub> O	21.7	-8.9	-16.9	-23.8	-30.2	-36.1	-47.3	-51.3
(21)	2NiS <sub>2</sub> + 8NaOH = 2Ni + 3Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>4</sub> + 4 H <sub>2</sub> O	-2.2	-64.5	-81.9	-98.0	-113.0	-127.2	-154.8	-165.9
(22)	2Ni <sub>3</sub> S <sub>2</sub> + 8NaOH = 6Ni + 3Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>4</sub> + 4 H <sub>2</sub> O	28.4	7.3	1.3	-4.2	-7.6	-9.9	-13.1	-14.3
(23)	2CoS + 8NaOH = 4Co + 3Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>4</sub> + 4 H <sub>2</sub> O	33.2	4.5	-3.3	-10.5	-17.1	-23.4	-35.6	-40.6
(24)	2CoS <sub>2</sub> + 8NaOH = 2Co + 3Na <sub>2</sub> S + Na <sub>2</sub> SO <sub>4</sub> + 4 H <sub>2</sub> O	18.6	-44.7	-62.4	-78.7	-94.0	-108.6	-136.9	-148.4

Table 5.  $\Delta G$  of reactions of interaction of iron sulfides with alkali, kJ/g-Fe atom

Reaction	$\Delta G^\circ$ at temperature, K:							
	298	373	573	673	773	973	1173	1273
$\text{FeS} + 2\text{NaOH} = \text{Fe} + 0,75\text{Na}_2\text{S} + 0,25\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	49.2	39.2	20.5	16.7	14.2	10.5	7.19	4.8
$\text{FeS} + 2\text{NaOH} = \text{FeO} + \text{Na}_2\text{S} + \text{H}_2\text{O}$	32.3	20.9	-1.8	-7.3	-11.5	-18.3	-23.9	-26.9
$\text{FeS} + 2\text{NaOH} = \text{Fe}(\text{OH})_2 + \text{Na}_2\text{S}$	15.2	15.1	21.6	30.3	39.8	59.8	80.0	89.7
$\text{FeS}_2 + 4\text{NaOH} = \text{Fe} + 1,5\text{Na}_2\text{S} + 0,5\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$	53.3	30.0	-20.7	-36.3	-49.6	-73.5	-96.2	-108.9
$\text{FeS}_2 + 4\text{NaOH} = \text{FeO} + 1,75\text{Na}_2\text{S} + 0,25\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$	36.4	11.7	-43.0	-60.3	-75.3	-102.4	-127.4	-140.6
$\text{FeS}_2 + 4\text{NaOH} = \text{Fe}(\text{OH})_2 + 1,75\text{Na}_2\text{S} + 0,25\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	19.3	5.9	-19.6	-22.7	-23.9	-24.2	-23.4	-24.0

Table 6.  $\Delta G_{623}$  of reactions of possible interaction between iron sulfides and arsenic pyrite with alkali (NaOH)

№	Reaction	$\Delta G_{623}$ , kJ/mol
(25)	$\text{FeS}_2 + 2\text{NaOH} = \text{Fe}(\text{OH})_2 + \text{Na}_2\text{S} + \text{S}^0$	81.7
(26)	$\text{FeS}_2 + 2\text{NaOH} = \text{FeO} + \text{H}_2\text{O} + \text{Na}_2\text{S} + \text{S}$	39.7
(27)	$\text{FeS}_2 + 4\text{NaOH} = \text{FeO} + 1,75\text{Na}_2\text{S} + 0,25\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$	-44.0
(28)	$\text{FeS} + 2\text{NaOH} = \text{Fe}(\text{OH})_2 + \text{Na}_2\text{S}$	37.4
(29)	$\text{FeS} + 2\text{NaOH} = \text{FeO} + \text{H}_2\text{O} + \text{Na}_2\text{S}$	-4.57
(30)	$\text{FeAsS} + 2\text{NaOH} = \text{Fe}(\text{OH})_2 + \text{Na}_2\text{S} + \text{As}^0$	48.8
(31)	$\text{FeAsS} + 2\text{NaOH} = \text{FeO} + \text{H}_2\text{O} + \text{Na}_2\text{S} + \text{As}^0$	6.81
(32)	$\text{FeS}_2 + 4\text{NaOH} + 3,5\text{O}_2 = \text{FeO} + 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$	-1452.2
(33)	$\text{FeS}_2 + 4\text{NaOH} + 3,75\text{O}_2 = 0,5\text{Fe}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$	-1557.8
(34)	$\text{FeS} + 2\text{NaOH} + 2\text{O}_2 = \text{FeO} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	-809.3
(35)	$\text{FeS} + 2\text{NaOH} + 2,25\text{O}_2 = 0,5\text{Fe}_2\text{O}_3 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	-914.85
(36)	$\text{FeAsS} + 2\text{NaOH} + 3,5\text{O}_2 = \text{FeAsO}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$	-1302.3
(37)	$\text{FeAsS} + 5\text{NaOH} + 3,5\text{O}_2 = 0,5\text{Fe}_2\text{O}_3 + \text{Na}_3\text{AsO}_4 + \text{Na}_2\text{SO}_4 + 2,5\text{H}_2\text{O}$	-1576.2

impossible. Accumulation of element sulfur in the alkaline melt of sulfur is, in its turn, accompanied by disproportionation reaction, e.g. (27). Its probability is estimated by value  $\Delta G_{623} = -44$  kJ/mol. Dissociative decomposition of pyrrhotine in alkaline melt to produce oxide of ferrous iron (29) is quite feasible as compared to the processes completing in formation of  $\text{Fe}(\text{OH})_2$  (28). Dissociative decomposition arsenic pyrite was also analyzed in two versions: with formation of hydroxide (30) and oxide (31) of ferrous iron, and element arsenic. In the case of iron oxide formation (II) analogy of increasing probability of chalcogenide dissociation can be observed. It would be noted, that irreversible nature of reactions (26), (29) and (31) is determined by formation of water and its removal from the system.

Under actual conditions of interaction in chalcogenide-alkali system probable is participation of oxygen intensively absorbed by molten alkali. Sulfide and element sulfur are fairly active reducing

agents and in the presence of oxygen are capable of transforming into sulfate sulfur. From Table 6 it follows, that decomposition of iron chalcogenides accompanied by redox reactions and transforming sulfur and arsenic into oxidation state +6 and +5, respectively, and iron – into oxidation state +3 with formation of oxide is thermodynamically quite probable. Sulfur and arsenic form alkali-soluble sodium sulfates and arsenates (33), (35) и (37). Solubility of  $\text{Na}_3\text{AsO}_4$  depends, at this, on temperature and material composition of the alkaline melt.

### Conclusions

1. Block-diagram of processing sulfide mineral raw materials for heavy non-ferrous metals has been analyzed.
2. Essence of metal reduction from metallurgical enrichment products and their arrangement have been studied.
3. Theoretical fundamentals of metal reduction have been analyzed.
4. Results of thermodynamic study of metal reduction in “metal sulfide-NaOH” system are presented.

### References

- [1] Тарасов А.В. *Производство цветных металлов и сплавов*. Справочник в 3 т. Т. 2. Производство тяжелых цветных металлов. М.: Metallurgiya, 2001. 408 с. [Tarasov A.V. *Fabrication of non-ferrous metals and alloys*. Handbook in 3 volumes. V. 2. Fabrication of heavy non-ferrous metals. Moscow, Metallurgiya, 2001, 408 p. (in Russian)]
- [2] Чекушин В.С., Борбат В.Ф. *Экстракция благородных металлов сульфидами и сульфоксидами*. М.: Наука, 1984. 164 с. [Chekushin V.S., Borbat V.F., *Extraction of noble metals by sulfides and sulfoxides*. Moscow, Nauka, 1984, 164 p. (in Russian)]
- [3] Гурьянова Е.Н., Гольдштейн И.П., Ромм И.П. *Донорно-акцепторная связь*. М.: Химия, 1973. 400 с. [Guriyanova E.N., Goldshtein I.P., Romm I.P. *Donor-acceptor bond*. Moscow, Khimiya, 1973, 400 p. (in Russian)]
- [4] Байков А.А. Сб. трудов: в 2 т. М., 1948. Т. 1.с. 151 – 160. [Baikov A.A. Collection of papers in 2 volumes. Moscow, 1948, V.1, 151-160 (in Russian)]
- [5] Есин О.А., Гельд П.В. *Физическая химия пирометаллургических процессов*: в 2–частях. Ч. 1.М.: Metallurgizdat, 1962. 703 с. [Esin O.A., Geld P.V. *Physical chemistry of pyrometallurgical processes*: in 2 parts. P. 1. Moscow, Metallurgizdat, 1962, 703 p. (in Russian)]
- [6] Волькенштейн Ф.Ф. *Физико-химия поверхности полупроводников*. М.: Наука, 1973. 399 с. [Volkenshtein F.F. *Physicochemistry of semiconductor surface*. Moscow, Nauka, 1973, 399 p. (in Russian)]
- [7] Чуфаров Г.И., Татиевская Е.П. *Физико-химические основы доменного процесса и современная практика производства чугуна*. Свердловск: Metallurgizdat, 1956. 646 с. [Chufarov G.I., Tatievskaya E.P. *Physics and chemistry of blast-furnace smelting operation and current practice of cast iron production*. Sverdlovsk, Metallurgizdat, 1956, 646 p. (in Russian)]
- [8] Вольский А.Н., Сергиевская Е.М. *Теория металлургических процессов*. М.: Metallurgiya, 1968. 244 с. [Volskiy A.N., Sergievskaya E.M. *Theory of metallurgical processes*. Moscow, Metallurgiya, 1968, 244 p. (in Russian)]

[9] Хауффе К. *Реакции в твердых телах и на их поверхности*. М.: Издательство иностранной литературы, 1963. 658 с. [Hauffe K. *Reactions in solid bodies and on their surface*. Moscow, Izdatelstvo inostrannoy literatury, 1963, 658 p. (in Russian)]

[10] Дей К., Селбин Д. *Теоретическая неорганическая химия*. М.: Химия, 1969. 432 с. [Dei K., Selbin D. *Theoretical inorganic chemistry*. Moscow, Khimiya, 1969, 432 p. (in Russian)]

[11] Чекушин В.С., Олейникова Н.В. Современные пирометаллургические технологии переработки сырья тяжелых цветных металлов. *Технология металлов*, 2007,(10), 8-13 [Chekushin V.S., Oleinikova N.V. Current pyrometallurgical processes in heavy metal raw material conversion. *Technology of metals*, 2007, 10, 8-13 (in Russian)]

[12] Алабышев А.Ф., Грачев К.Я., Зарецкий С.А., Лантратов М.Ф. *Натрий и калий (получение, свойства, применение)*. Л.: Госхимиздат, 1959. 391 с. [Alabyshev A.F., Grachev K.Ya., Zaretskiy S.A. Lantrapov M.F. *Sodium and potassium (production, properties, application)*. Leningrad, Goshimizdat, 1959, 391 p. (in Russian)]

[13] Лаптев Ю.В. Сиркис Л.А., Колонин Г.Р. *Сера и сульфидообразование в гидрометаллургических процессах*. Новосибирск: Наука, 1987. 160 с. [Laptev Yu.V., Sirkis L.A., Kolonin G.R. *Sulfur and sulfide formation in hydrometallurgical processes*. Novosibirsk, "Nauka", 1987, 160 p. (in Russian)]

[14] Oleinikova N.V. Chekushin V. S., Baksheev S. P.Reduction of metals from sulfides. *Russian Journal of Non-Ferrous Metals*, 2007, 48 (2), 88–91.

[15] Чекушин В.С., Олейникова Н.В. Термодинамика и кинетика процессов разложения халькогенидов железа в щелочных средах. *Технология металлов*. 2007, 11, 2–7 [Chekushin V.S., Oleinikova N.V. Thermodynamics and kinetics of iron chalcogenide decomposition in alkaline media, *Technology of metals*, 2007, (11), 2-7 (in Russian)]